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[Title of the Invention] TONER AND IMAGE-FORMING APPARATUS USING THE TONER

[Claims]

[Claim 1] A toner, which is manufactured by performing in the order of: (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; and (2) a process of externally adding positively electrifiable silica fine particles.

[Claim 2] The toner as claimed in claim 1, wherein the negatively electrifiable silica fine particles comprise two kinds of negatively electrifiable silica fine particles each having a different average particle size, and the addition ratio of the negatively electrifiable silica fine particles having a large average particle size to the negatively electrifiable silica fine particles having a small average particle size is 1/3 to 3/1 in a mass ratio.

[Claim 3] The toner as claimed in claim 1 or 2, wherein the negatively electrifiable silica fine particles and the positively electrifiable silica fine particles are externally added in a mass ratio of from 1/1 to 30/1.

[Claim 4] An image-forming apparatus which is stocked with the toner as claimed in any of claims 1 to 3.

[Claim 5] The image-forming apparatus as claimed in claim 4, which is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a toner which is used for developing an electrostatic latent image in electrophotography, electrostatic recording and electrostatic printing and for forming an image by thermal fixation, and also relates to an image-forming apparatus using the toner.

[0002]

[Background Art]

The toner for forming electrostatic images generally comprises, as the toner mother particles, fine particles of a binding resin containing a coloring component, e.g., a dye or a pigment, and, if necessary, an electrification controlling agent, and the toner is manufactured by a method of adding external additives to the outside

(surface) of the toner mother particles for the purpose of providing flowability or controlling an electrification property. As the external additives, positively electrifiable silica fine particles, negatively electrifiable silica fine particles, inorganic fine particles other than silica (e.g., titanium oxide), fatty acid metal salt and the like are used.

[0003]

For example, a toner comprising toner mother particles having externally added thereto positively electrifiable hydrophobic silica fine particles, a toner comprising toner mother particles having externally added thereto positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles, a toner comprising toner mother particles having externally added thereto positively electrifiable hydrophobic silica fine particles and inorganic fine particles having a low electrical resistance value (e.g., metallic oxide inorganic particles, e.g., titanium oxide) (these toners are disclosed in patent literature 1 and 2), and a toner comprising toner mother particles having externally added thereto two kinds of positively electrifiable substances (e.g., silica) each having different particle size and inorganic fine particles (patent

literature 3) are known. In patent literature 1 to 3, negatively electrifiable binding resins are used.

[0004]

Also, a toner being externally adding positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles to a toner mother particle (refer to, e.g., patent literature 4), and a toner having a excellent charge rising property which is produced by a method of externally adding a first component, a second component, a third component and a fourth component to toner mother particles at the same time, or externally adding the first component lastly, taking hydrophobic silica fine particles or hydrophobic titania as the first component, hydrophobic silica fine particles or hydrophobic titania having larger particle sizes than the particle sizes of component 1 as the second component, inorganic fine particles as the third component, and a fatty acid metal salt as the fourth component (refer to, e.g., patent literature 5) are known.

[0005]

Further, there is disclosed in a patent literature a method to obtain a toner in which the liberation of external additives is restrained by externally adding in the order of titanium oxide fine particles and silica fine

particles to toner mother particles (refer to, e.g., patent literature 6).

[0006]

However, in the toners obtained by the methods disclosed in patent literature 1 to 6, external additives (positively electrifiable silica fine particles, negatively electrifiable silica fine particles, titanium oxide fine particles and the like), which function to control electrification or flowability, are liable to be desorbed from the surface of the toner, which causes the reduction of flowability or electrification property of the toners, as a result, transfer efficiency and image density are depressed.

[0007]

[Patent literature 1]

JP-A-2000-267337 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

[Patent literature 2]

JP-A-2002-14487

[Patent literature 3]

JP-A-2002-214834

[Patent literature 4]

JP-A-11-231571

[Patent literature 5]

JP-A-2001-100452

[Patent literature 6]

JP-A-2002-72544

[Patent literature 13]

JP-A-2002-202622

[0008]

[Problems to be Resolved by the Invention]

An object of the invention is to provide a toner which is low in desorption of positively electrifiable silica fine particles, negatively electrifiable silica fine particles, which can maintain the electrification property for a long period of time, shows high flowability and transfer efficiency.

[0009]

[Means of Solving the Problems]

The present invention provides a toner which is manufactured by performing in the order of (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; and (2) a process of externally adding positively electrifiable silica fine particles.

[0010]

In a preferred embodiment of the present invention, the negatively electrifiable silica fine particles comprise two kinds of negatively electrifiable silica fine particles

each having a different average particle size, and the addition ratio of the negatively electrifiable silica fine particles having a large average particle size to the negatively electrifiable silica fine particles having a small average particle size is 1/3 to 3/1 in a mass ratio.

[0011]

In another preferred embodiment of the present invention, the negatively electrifiable silica fine particles and the positively electrifiable silica fine particles are externally added in a mass ratio of from 1/1 to 30/1.

[0012]

The present invention further provides an image-forming apparatus which is stocked with any of the above-described toners.

[0013]

In a preferred embodiment of the present invention, the image-forming apparatus is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[0014]

[Detailed Description of the Preferred Embodiment]

The toner of the present invention is manufactured by adding negatively electrifiable silica fine particles to toner mother particles, and then adding positively electrifiable silica fine particles. In the specification of the invention, materials externally added to toner mother particles, e.g., negatively electrifiable silica fine particles and positively electrifiable silica fine particles, and if necessary, titanium oxide fine particles, particles comprising a long chain fatty acid or a salt thereof, and inorganic fine particles, are referred to as external additives, and adding these external additives to the exteriors (surfaces) of toner mother particles is called external addition.

[0015]

The materials which are used in the invention, e.g., (i) toner mother particles and the materials constituting the toner mother particles (so-called internal additives, e.g., binding resins, colorants, mold releasing agents, dispersants, electrification controlling agents, and magnetic agents), (ii) negatively electrifiable silica fine particles, (iii) positively electrifiable silica fine particles, (iv) titanium oxide fine particles, (v) long chain fatty acids or salts thereof, and (vi) inorganic fine

particles which are added according to necessity, are described in the first place, and then the toner of the present invention is described.

[0016]

(I) Materials which are used in the present invention:

(i) Toner mother particles:

Toner mother particles contain a binding resin and a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent.

[0017]

(Binding resin)

As binder resins, resins which are ordinarily used as the materials of toners are used. As such resins, polystyrene-based resins, acrylate-based resins or methacrylate-based resins (hereinafter referred to as (meth)acrylate-based resins), styrene-acrylic-based resins, polyester resins, polyethylene resins, epoxy resins, silicone resins, polypropylene resins, fluorine resins, polyamide resins, polyvinyl alcohol resins, polyurethane resins, polyvinyl butyral resins, and copolymers containing the constituents of these resins are used.

[0018]

Among them, polystyrene-based resins and styrene-(meth)acrylate-based resin copolymers are preferably used.

[0019]

As polystyrene resins, e.g., hydrogenated styrene resins, styrene-isobutylene copolymers, acrylonitrile-butadiene-styrene copolymers (ABS resins), acrylonitrile-styrene copolymers (AS resins), acrylonitrile-polyethylene chloride-styrene copolymers (ACS resins), styrene-p-chlorostyrene copolymers, styrene-propylene copolymers, styrene-butadiene crosslinked polymers, styrene-butadiene-chlorinated paraffin copolymers, styrene-allyl alcohol copolymers, styrene-butadiene rubbers, styrene-maleic ester copolymers, styrene-isobutylene copolymers, and styrene-maleic anhydride copolymers are exemplified.

[0020]

As styrene-(meth)acrylate-based resin copolymers, e.g., acrylate-styrene-acrylonitrile copolymers (ASA resins), styrene-diethylaminoethyl methacrylate copolymers, styrene-methyl methacrylate copolymers, styrene-n-butyl methacrylate copolymers, styrene-methyl methacrylate-n-butyl acrylate copolymers, styrene-methyl methacrylate-butyl allylate-N-(ethoxymethyl)acrylamide copolymers, styrene-glycidyl methacrylate copolymers, styrene-butadiene-dimethylaminoethyl methacrylate copolymers, styrene-acrylate-maleate copolymers, styrene-methyl methacrylate-2-ethylhexyl acrylate copolymers, styrene-n-butyl allylate-ethyl glycol methacrylate copolymers,

styrene-n-butyl methacrylate-acrylic acid copolymers, styrene-n-butyl methacrylate-maleic anhydride copolymers, styrene-butyl acrylate-isobutylmaleic half ester-divinylbenzene copolymers, styrene-butadiene-acrylate copolymers, and styrene-acrylate copolymers are exemplified.

[0021]

When a toner is fixed by thermal fixation in image formation, the flow softening point (Tm) of a binding resin is preferably low. Tm is preferably from 85 to 140° C, more preferably from 90 to 120°C, and still more preferably from 100 to 110°C. The glass transition temperature (Tg) of a binding resin is preferably from 40 to 90°C, more preferably from 50 to 80°C. A flow softening point (Tm) is measured by using a sample obtained by pressure-molding 1.0 g of a binding resin to make a pellet, with "Flow Tester CFT-500D" (a product of Shimadzu Corporation) on conditions of: heat-up velocity of 5°C/min; cylinder pressure of 2.0 MPa; the hole diameter of a die of 1.0 mm; the hole length of a die of 1.0 mm; and by Tm computing method of a 1/2 method. Further, the glass transition temperature (Tg) of a binding resin is measured by packing 10 mg of a binding resin in an aluminum cell and with "DSC120" (a product of Seiko Instruments Inc.) on conditions of: measuring temperature of from 0 to 200°C;

and heat-up velocity of 10°C/min; and the value is read from the DSC curve of the second heat-up time.

[0022]

When a toner is fixed by pressure fixation, wax-like resins are preferably used as the binding resin. Of the above binding resins, polyethylene resins, polyethylene-vinyl acetate copolymers and natural waxes are used as the wax-like resins.

[0023]

The binding resins are manufactured by polymerization, e.g., emulsion polymerization, dispersion polymerization and suspension polymerization, or pulverization including kneading, pulverization and classification processes. Considering the homogeneity and flowability of the finally obtained toner particles, the binding resins obtained by polymerization are preferably used.

[0024]

The binding resins may be used alone or two or more binding resins may be blended. The above-shown binding resins are representative examples and the present invention is not of course limited thereto.

[0025]

(Colants)

As colorants, the following-shown organic pigments,

inorganic pigments and dyes are used. Of organic and inorganic pigments, carbon black, copper oxide, tri-iron tetroxide, manganese dioxide, Aniline Black and active carbon are used as black pigments.

[0026]

As yellow pigments, chrome yellow, zinc yellow, cadmium yellow, yellow iron oxide, mineral fast yellow, nickel titan yellow, naples yellow, Naphthol Yellow S, Hansa Yellow, Benzidine Yellow G, Benzidine Yellow GR, Quinoline Yellow Lake, Permanent Yellow NCG, and Tartrazine Lake are used.

[0027]

As orange pigments, red chrome yellow, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange RK, Benzidine Orange G, and Indanthrene Brilliant Orange GKM are used.

[0028]

As red pigments, iron oxide red, cadmium red, red lead, mercury sulfide, cadmium, Permanent Red 4R, Lithol Red, Pyrazolone Red, Watchung Red, calcium salt, Lake Red D, Brilliant Carmine 6B, eosine lake, Rhodamine Lake B, Alizarine Lake and Brilliant Carmine 3B are used.

[0029]

As violet pigments, manganese violet, Fast Violet B and Methyl Violet Lake are used. As blue pigments,

Prussian blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, nonmetal Phthalocyanine Blue, partially chlorinated product of Phthalocyanine Blue, Fast Sky Blue and Indanthrene Blue BC are used.

[0030]

As green pigments, chrome green, chromium oxide, Pigment Green B, Malachite Green Lake and Final Yellow Green G are used.

[0031]

As white pigments, zinc flower, titanium oxide, antimony white and zinc sulfide are used.

[0032]

As extender pigments, baryta powder, barium carbonate, clay, silica, white carbon, talc and alumina white are used.

[0033]

As dyes, basic dyes, acid dyes, dispersed dyes and direct dyes are used. The examples of such dyes include Nigrosine, Methylene Blue, Rose Bengale, Quinoline Yellow and Ultramarine Blue.

[0034]

When the toner of the present invention is a transparent color toner, the following-shown various pigments and dyes are used as the colorants.

[0035]

As yellow pigments, C.I. 10316 (Naphthol Yellow S), C.I. 11710 (Hansa Yellow 10G), C.I. 11660 (Hansa Yellow 5G), C.I. 11670 (Hansa Yellow 3G), C.I. 11680 (Hansa Yellow G), C.I. 11730 (Hansa Yellow GR), C.I. 11735 (Hansa Yellow A), C.I. 11740 (Hansa Yellow NR), C.I. 12710 (Hansa Yellow R), C.I. 12720 (Pigment Yellow L), C.I. 21090 (Benzidine Yellow), C.I. 21095 (Benzidine Yellow G), C.I. 21100 (Benzidine Yellow GR), C.I. 20040 (Permanent Yellow NCG), C.I. 21220 (Vulcan Fast Yellow 5) and C.I. 21135 (Vulcan Fast Yellow R) are used.

[0036]

As red pigments, C.I. 12055 (Stirling I), C.I. 12075 (Permanent Orange), C.I. 12175 (Lithol Fast Orange 3GL), C.I. 12305 (Permanent Orange GTR), C.I. 11725 (Hansa Yellow 3R), C.I. 21165 (Vulcan Fast Orange GG), C.I. 21110 (Benzidine Orange G), C.I. 12120 (Permanent Red 4R), C.I. 1270 (Para Red), C.I. 12085 (Fire Red), C.I. 12315 (Brilliant Fast Scarlet), C.I. 12310 (Permanent Red F2R), C.I. 12335 (Permanent Red F4R), C.I. 12440 (Permanent Red FRL), C.I. 12460 (Permanent Red FRLL), C.I. 12420 (Permanent Red F4RH), C.I. 12450 (Light Fast Red Toner B), C.I. 12490 (Permanent Carmine FB), and C.I. 15850 (Brilliant Carmine 6B) are used.

[0037]

As blue pigments, C.I. 74100 (nonmetal

Phthalocyanine Blue), C.I. 74160 (Phthalocyanine Blue), and C.I. 74180 (Fast Sky Blue) are used.

[0038]

These colorants may be used alone or a plurality of colorants may be used in combination. The colorants are used in an amount of from 1 to 20 mass% to 100 mass% of the binding resin, preferably from 2 to 10 mass%. When the amount of colorants is more than 20 mass%, the fixing property and transparency of the toner decrease, while when the amount is less than 1 mass%, there is a risk of incapable of obtaining desired image density.

[0039]

(Mold releasing agents)

As the mold releasing agent, paraffin-based waxes, polyolefin-based waxes, modified waxes having an aromatic group, hydrocarbon compounds having an alicyclic group, natural waxes, long chain fatty acids having 12 or more carbon atoms, the esters thereof, metal salts of long chain fatty acids (metal soaps), fatty acid amide and fatty acid bisamide are used. Of the above mold releasing agents, paraffin-based waxes, polyolefin-based waxes and metal soaps are preferably used.

[0040]

The examples of paraffin-based waxes include, e.g., paraffin wax (manufactured by Nippon Oil Co., Ltd. and

Nippon Seiro Co., Ltd.), micro-wax (manufactured by Nippon Oil Co., Ltd.), micro-crystalline wax (manufactured by Nippon Seiro Co., Ltd.), hard paraffin wax (manufactured by Nippon Seiro Co., Ltd.), PE-130 (manufactured by Hoechst A.G.), Mitsui High Wax 110P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 220P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 660P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 210P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 320P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 410P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 420P (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-2130 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-4020 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-5020 (manufactured by Mitsui Petrochemical Industries, Ltd.), beeswax, carnauba wax and montan wax.

[0041]

As polyolefin-based waxes, e.g., low molecular weight polypropylene, low molecular weight polyethylene,

oxidation type polypropylene and oxidation type polyethylene are exemplified. The specific examples of polyolefin-based waxes include non-oxidation type polyethylene waxes, e.g., Hoechst Wax PE520, Hoechst Wax PE130, Hoechst Wax PE190 (manufactured by Hoechst A.G.), Mitsui High Wax 200, Mitsui High Wax 210, Mitsui High Wax 210M, Mitsui High Wax 220, Mitsui High Wax 220M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX 131-P, SANWAX 151-P, and SANWAX 161-P (manufactured by Sanyo Chemical Industries Co., Ltd.), oxidation type polyethylene waxes, e.g., Hoechst Wax PED121, Hoechst Wax PED153, Hoechst Wax PED521, Hoechst Wax PED522, Hoechst Wax Ceridust 3620, Hoechst Wax Ceridust VP130, Hoechst Wax Ceridust VP5905, Hoechst Wax Ceridust VP9615A, Hoechst Wax Ceridust TM9610F, Hoechst Wax Ceridust 3715 (manufactured by Hoechst A.G.), Mitsui High Wax 420M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX E-300 and SANWAX E-250P (manufactured by Sanyo Chemical Industries Co., Ltd.), non-oxidation type polypropylene waxes, e.g., Hoechst Wachs PP230 (manufactured by Hoechst A.G.), and VISCOL 330-P, VISCOL 550-P, VISCOL 660-P (manufactured by Sanyo Chemical Industries Co., Ltd.), and oxidation type polypropylene waxes, e.g., VISCOL TS-200 (manufactured by Sanyo Chemical Industries Co., Ltd.).

[0042]

These mold releasing agents may be used alone or a plurality of compounds may be used in combination. Mold releasing agents having a low softening point (melting point), e.g., from 40 to 130°C, preferably from 50 to 120°C, are preferably used. A softening point is represented by an endothermic main peak value on the DSC endothermic curve measured with "DSC120" (a product of Seiko Instruments Inc.).

[0043]

As the examples of fatty acid metal salts (metal soaps), e.g., zinc stearate, calcium stearate, magnesium stearate, zinc oleate, zinc palmitate and magnesium palmitate are preferably used.

[0044]

(Dispersants)

Metal soaps and polyethylene glycol and the like are used as the dispersant.

[0045]

(Electrification controlling agents)

A electrification controlling agent is not particularly limited unless it provides a positive charge or a negative charge by friction-charging. An organic electrification controlling agent or an inorganic electrification controlling agent can be used. As the positive electrification controlling agents, commercially

available products are used. For example, Nigrosine Base EX (manufactured by Orient Chemical Industry Co., Ltd.), a quaternary ammonium salt P-51 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine Bontoron N-01 (manufactured by Orient Chemical Industry Co., Ltd.), Sudan Chief Schwarz BB (Solvent Black 3: Color Index 26150), Fetschwarz HBN (C.I. No. 26150), Brilliant Spirits Schwarz TN (manufactured by Farbenfabriken Bayer A.G.), and Zaponschwarz X (manufactured by Farberke Hoechst A.G.) are exemplified. Of these products, a quaternary ammonium salt P-51 is preferably used. In addition to the above products, alkoxylated amine, alkylamide and chelate pigments of molybdic acids are also used as a positive electrification controlling agent. These positive electrification controlling agents may be used alone or a plurality of compounds may be used in combination.

[0046]

As negative electrification controlling agents, a commercially available negative electrification controlling agents can be used. For example, Oil Black (Color Index 26150), Oil Black BY (manufactured by Orient Chemical Industry Co., Ltd.), Bontron S-22 (manufactured by Orient Chemical Industry Co., Ltd.), salicylic acid metal complex E-81 (manufactured by Orient Chemical Industry Co., Ltd.), thioindigo series pigments, sulfonylamine derivatives of

copper phthalocyanine, Spiron Black TRH (manufactured by HODOGAYA CHEMICAL Co., Ltd.), Bontoron S-34 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine SO (manufactured by Orient Chemical Industry Co., Ltd.), Celesschwarz (R)G (manufactured by Farbenfabriken Bayer A.G.), Chromogeneschwarz ETOO (C.I. No. 14645), and Azo Oil Black (R) (manufactured by National Aniline Co.). Of these products, salicylic acid metal complex E-81 is preferably used. These negative electrification controlling agents can be used alone or a plurality of compounds may be used in combination.

[0047]

(Magnetic agents)

As magnetic agents, metallic powders of, e.g., Fe, Co, Ni, Cr, Mn and Zn, metallic oxides, e.g., Fe_3O_4, Fe_2O_3, Cr_2O_3, ferrite, and alloys showing ferromagnetism by thermal treatment, e.g., alloys containing manganese and acid, are exemplified. These magnetic agents may be subjected to treatment in advance with a coupling agent.

[0048]

(Manufacture of toner mother particles)

Toner mother particles are manufactured by adding a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent, to a binding resin.

A method of manufacturing mother particles by a pulverizing method including kneading, pulverization and classification processes is described below. Firstly, a binding agent, a colorant and additives, e.g., a mold releasing agent, in prescribed amounts are introduced into a mixer, e.g., Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED) and blended homogeneously. The blending ratios of additives, e.g., a binding resin, a colorant, an electrification controlling agent, and a mold releasing agent, are decided arbitrarily taking the color and electrification property of the toner into consideration.

[0049]

The above mixture is then introduced into a twin-screw kneading extruder (PCM-30, manufactured by IKEGAI KASEI CO., LTD) and homogeneously melt kneaded. As the melt-kneading means besides the above, continuous kneaders, e.g., "TEM-37" (manufactured by TOSHIBA MACHINE CO., LTD.) and "KRC Kneader" (manufactured by KURIMOTO, LTD.), and batch type kneaders, e.g., a hot-pressing kneader, are exemplified. Toner mother particles having a desired average particle size can be obtained by pulverizing the obtained melt-kneaded product by means of a grinding means. Pulverization is performed by, e.g., impinging pulverization by jet air using a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION) or IDS-2 (a product

of Nippon Pneumatic Mfg Co., Ltd.), in addition, by a mechanical pulverizer Turbo Mill (a product of Kawasaki Heavy Industries, Ltd.) or Super Rotor (a product of Nisshin Engineering), etc.

[0050]

In the next place, the particle size of the obtained toner mother particles is adjusted by wind power or rotation of rotors. For instance, a sharp particle size distribution can be obtained by using, e.g., a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), DSX-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), or Elbow-Jet (a product of NITTETSU MINING CO., LTD.).

[0051]

Toner mother particles may also be manufactured by a method of dissolving internal additives constituting the toner mother particles, e.g., a resin and a colorant, in an organic solvent, dispersing and granulating the aqueous solvent with a classifying agent and an emulsifying agent, and then separating and drying the emulsion.

[0052]

(ii) Negatively electrifiable silica fine particles:

Negatively electrifiable silica fine particles which are used in the present invention are not particularly restricted. Negatively electrifiable silica fine particles

having an average particle size of from 4 to 120 nm, preferably from 5 to 50 nm, and more preferably from 6 to 40 nm are generally used. The smaller the average particle size of negatively electrifiable silica fine particles, the higher is the flowability of the toner obtained. When the average particle size is smaller than 4 nm, the negatively electrifiable silica fine particles are liable to be buried in the toner mother particles. When the average particle size is larger than 120 nm, there is the possibility of conspicuous degradation of the flowability. In the specification of the invention, the terminology "average particle size" of the fine particles of negatively electrifiable silica, positively electrifiable silica, toner mother particles and toner particles means a volume average particle size, unless otherwise indicated.

[0053]

It is preferred that negatively electrifiable silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of negatively electrifiable silica fine particles hydrophobic, the flowability and electrification property of the toner are further improved. The hydrophobitization treatment of silica fine particles is carried out according to wet methods or dry methods usually used in the industry with a silane compound, e.g., aminosilane, hexmethyldisilazane, or dimethyldicyclosilane;

or a silicone oil, e.g., dimethylsilicone, methylphenylsilicone, fluorine-modified silicone oil, alkyl-modified silicone oil, amino-modified silicone oil, or epoxy-modified silicone oil.

[0054]

As negatively electrifiable hydrophobic silica fine particles, commercially available RX200 and RX50 (manufactured by Nippon Aerosil Co., Ltd.) and TG811F, TG810G and TG308F (manufactured by Cabot) are used.

[0055]

(iii) Positively electrifiable silica fine particles:

Positively electrifiable silica fine particles which are used in the present invention are not especially limited. The volume average particle size of positively electrifiable silica fine particles is preferably from 10 to 50 nm, more preferably from 15 to 40 nm, taking the flowability and the like into consideration.

[0056]

It is preferred that positively electrifiable silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of positively electrifiable silica fine particles hydrophobic, the flowability and chargeability of the toner can be improved. The hydrophobitization of positively electrifiable silica fine particles is carried out according to the same method as

the hydrophobitization of negatively electrifiable silica fine particles.

[0057]

As positively electrifiable hydrophobic silica fine particles, commercially available NA50H (manufactured by Nippon Aerosil Co., Ltd.) and TG820F (manufactured by Cabot) are used.

[0058]

(iv) Titanium oxide (titania) fine particles:

Titanium oxide fine particles for use in the present invention are not particularly limited. Titanium oxide fine particles having a relatively small electrical resistivity are preferably used. Titanium oxide may take a crystal form of rutile type, anatase type, rutile-anatase type. Titanium oxide of any crystal form may be used, but titanium oxide of a rutile-anatase type is preferably used for the reason that the adjustment of electric charge is easy and a rutile-anatase type titanium oxide is difficult to be buried in toner mother particles even when the number of sheets of printing increases.

[0059]

The size of titanium oxide fine particles is not particularly restricted but it is preferred that the particle size or long axis length be 10 to 30 nm. In the case of a rutile-anatase type titanium oxide, titanium

oxide fine particles having a long axis length of about 20 nm are preferred.

[0060]

By making the surfaces of titanium oxide fine particles hydrophobic, a stable electrification property can be maintained, and the flowability of the toner can be improved. The hydrophobitization of titanium oxide fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0061]

As hydrophobic titanium oxide fine particles, STT-30S (manufactured by TITAN KOGYO KABUSHIKI KAISHA) and the like are used.

[0062]

(v) Long chain fatty acid or salt thereof

The long chain fatty acids or salts thereof for use in the present invention according to need are not particularly restricted. As the long chain fatty acids, long chain fatty acids preferably having from 10 to 30 carbon atoms, more preferably from 12 to 28 are used. As the long chain fatty acids, long chain saturated fatty acids and long chain unsaturated fatty acids are exemplified. Long chain saturated fatty acids are preferably used. The long chain fatty acids may be

branched, but long chain saturated fatty acids, e.g., stearic acid, is preferably used.

[0063]

It is preferred to use the long chain fatty acids in the form of salts, and more preferably in the form of metal salts (so-called metal soaps). The metal salts of the long chain fatty acids are not particularly restricted and, e.g., calcium salts, zinc salts, magnesium salts, aluminum salts and lithium salts are exemplified. As the metal soaps, e.g., magnesium stearate, calcium stearate and zinc stearate are exemplified, and fine particles of these metal soaps are preferably used. Particles comprising long chain saturated fatty acids or salts thereof may be used alone or as mixtures of two or more kinds.

[0064]

(vi) Inorganic fine particles

Inorganic fine particles other than titanium oxide fine particles are also externally added for the purpose of controlling the electrification property and improving flowability. For instance, as inorganic fine particles, fine particles of metallic oxide, e.g., aluminum oxide, strontium oxide, tin oxide, zirconia oxide, magnesium oxide, and indium oxide; fine particles of nitrides, e.g., silicon nitride; fine particles of carbides, e.g., silicon carbide; fine particles of metal salts, e.g., calcium sulfate,

barium sulfate and calcium carbonate; and inorganic fine particles of these are exemplified. Fine particles of metallic oxides having a relatively small electrical resistivity, e.g., $10^9 \Omega\cdot cm$ or less are preferably used.

[0065]

The sizes of inorganic fine particles added are not particularly restricted, but the sizes of from 10 to 30 nm are preferred. It is preferred that the surfaces of these inorganic fine particles be subjected to hydrophobitization treatment for the purpose of improving the stabilization of electrification characteristics. The hydrophobitization treatment of inorganic fine particles is performed by the same method as used in the hydrophobitization treatment of negatively electrifiable silica fine particles or positively electrifiable silica fine particles.

[0066]

(II) Toner of the present invention and manufacturing method:

The toner in the invention is manufactured by performing in the order of (1) a process of externally adding negatively electrifiable silica fine particles to toner mother particles containing a binding resin and a colorant; and (2) a process of externally adding positively electrifiable silica fine particles.

[0067]

A method of manufacturing the toner of the present invention is described in further detail below. In process (1), negatively electrifiable silica fine particles are externally added to toner mother particles containing a binding resin and a colorant. In process (1), negatively electrifiable silica fine particles having a uniform average particle size may be used alone, but it is preferred to use two or more negatively electrifiable silica fine particles respectively having different average particle sizes in combination. In general, negatively electrifiable silica fine particles having a small average particle size (small particle size silica) are used, but when negatively electrifiable silica fine particles having a large average particle size (large particle size silica) are used in combination with small particle size silica, not only the absolute value of the quantity of electrification can be made great, but small particle size silica can be prevented from being buried in toner mother particles due to the resistance of large particle size silica, as compared with the case where small particle size silica is used alone, so that the stability of electrification of the toner can be ensured for a long period of time. Further, it becomes possible to improve the flowability of the toner, and improve the storage stability of the toner by the blocking effect against heat.

It is preferred to use negatively electrifiable silica fine particles having an average particle size of from 5 to 20 nm, preferably from 6 to 15 nm, as the small particle size silica and negatively electrifiable silica fine particles having an average particle size of from 20 to 50 nm, preferably from 20 to 40 nm, as the large particle size silica. In addition, the difference in average particle size between large particle size silica and small particle size silica is preferably 10 nm or more, and more preferably 20 nm or more.

[0068]

For the purpose of imparting flowability to a toner and ensuring the stability of electrification for a long period of time, the addition ratio of large particle size silica to small particle size silica in a mass ratio is from 1/3 to 3/1, preferably from 1/2 to 2/1, and more preferably from 1/1.5 to 1.5/1.

[0069]

Large particle size silica and small particle size silica may be blended at the same time, alternatively either silica particles may be added prior to the other.

[0070]

In the next place, positively electrifiable silica fine particles are externally added (process (2)). It is preferred that the surfaces of positively electrifiable

silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of positively electrifiable silica fine particles hydrophobic, the fluctuation of the electrification property of the toner due to the changes in external environment can be lessened, and the flowability of the toner can be improved.

[0071]

The addition amounts of negatively electrifiable silica fine particles and positively electrifiable silica fine particles used in the manufacture of a toner are not necessarily limited to the above weight ratio, since there is a case where the external addition amounts to be stuck around toner mother particles are adjusted according to the average particle size or the particle size distribution of toner mother particles.

[0072]

In the case of negatively electrifiable silica fine particles, e.g., the above small particle size silica is added in an amount of from 0.5 to 4.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.5 to 2 mass parts, and more preferably from 0.7 to 1.5 mass parts. In the case of large particle size silica, the addition amount is from 0.2 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.3 to 1.5 mass parts. When large particle size

silica and small particle size silica are used in combination, they are added in total amount of from 0.5 to 4 mass parts to 100 mass parts of the toner mother particles, preferably from 0.5 to 3 mass parts, and more preferably from 0.7 to 2.5 mass parts, taking the above-described blending ratio into consideration.

[0073]

Positively electrifiable silica fine particles are added in an amount of from 0.1 to 1.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.2 to 0.8 mass parts.

[0074]

In the present invention, the addition ratio of negatively electrifiable silica fine particles to positively electrifiable silica fine particles is not particularly restricted. However, considering the uniformity and stability of electrification of the toner obtained, the amount ratio of negatively electrifiable silica fine particles/positively electrifiable silica fine particles is preferably from 1/3 to 40/1, more preferably from 1/1 to 30/1, and still more preferably from 1/1 to 20/1. By adjusting the ratio of negatively electrifiable silica fine particles/positively electrifiable silica fine particles to this range, electric charge is adjusted, the liberation rate of silica is restrained, and the rate of

occurring of positively electrified toner is controlled, thus the uniformity of electrification, long term electrification stability and good flowability of the toner are brought about.

[0075]

On the other hand, when the ratio is smaller than 1/3, the influence of positively electrifiable silica becomes great, a negative electrification property cannot be adjusted well, the fluctuation of electric charge at use time with aging becomes great, and the electrification property cannot be maintained stably for a long period of time, and there is the possibility of the degradation of transfer efficiency. On the other hand, when the ratio is greater than 40/1, the uniformity of electrification of the toner is impaired, in addition, the liberation rate of silica fine particles becomes great. As a result, the fluctuation of electric charge at use time with aging becomes great and the electrification property cannot be maintained stably for a long period of time, and there is the possibility of the degradation of development efficiency and transfer efficiency.

[0076]

Since the addition amounts of negatively electrifiable silica fine particles and positively electrifiable silica fine particles to toner mother particles are

preferably respectively the above range, the ratio of negatively electrifiable silica fine particles/positively electrifiable silica fine particles may be decided in the preferred range of each addition amount.

[0077]

If necessary, (iv) titanium oxide fine particles, (v) a long chain fatty acid or a salt thereof, and (vi) inorganic fine particles may be added for the purpose of the adjustment of electric charge and the improvement of flowability. These external additives are preferably externally added after positively electrifiable silica fine particles have been added to toner mother particles, i.e., after process (2). The addition amounts of these external additives are selected so as not to hinder the characteristics of the toner of the present invention.

[0078]

External addition of negatively electrifiable silica fine particles and positively electrifiable silica fine particles to toner mother particles is carried out by machines or methods usually used in this industry, e.g., high speed fluid mixers, such as a Henschel mixer or Perpenmyer, and mixers using a mechanochemical method. The toner of the present invention can be obtained, for example, by putting toner mother particles and negatively electrifiable silica fine particles into a Henschel mixer

and stirring at a prescribed stirring velocity for prescribed time as the first stage process (process (1)), and introducing positively electrifiable silica fine particles and stirring at a prescribed stirring velocity for prescribed time as the second stage process (process (2)). The velocity and time of stirring in each process can be set independently, but the conditions may be the same. External additives added according to necessity are also added in the same manner.

[0079]

According to the manufacturing method of the toner of the present invention, since the static attraction between toner mother particles and negatively electrifiable silica fine particles is not hindered by adding negatively electrifiable silica fine particles alone in the first place in process (1), and the difference between the work function of negatively electrifiable silica fine particles and the work function of toner mother particles is large, negatively electrifiable silica fine particles can be strongly adhered to toner mother particles. Therefore, the desorption of negatively electrifiable silica fine particles is prevented and the fluctuation of electrification property lessens, as a result, an electrification property can be stabilized for a long period of time.

[0080]

Subsequently, positively electrifiable silica fine particles are externally added in process (2). Since the externally added positively electrifiable silica fine particles function as the electric charge adjuster, the electric charge per a toner is unified. Further, since the positively electrifiable silica fine particles come to be liberated and present in the toner in an appropriate rate, the flowability of the toner becomes good and, at the same time, the free positively electrifiable silica fine particles function as the carrier, so that the electrification property becomes more uniform.

[0081]

As a result of synergistic function of each effect of process (1) and process (2), good electrification uniformity, long term electrification stability and good flowability are brought about to the toner of the present invention.

[0082]

On the other hand, conventional toners, e.g., the toners disclosed in patent literature 1 to 4, are toners obtained by externally adding positively electrifiable silica fine particles and negatively electrifiable silica fine particles at the same time, and it is thought that by adding positively electrifiable silica fine particles and

negatively electrifiable silica fine particles at the same time, the static attraction between the toner mother particles and the negatively electrifiable silica fine particles becomes small, as a result, strong adhesion is hindered and the desorption of the negatively electrifiable silica fine particles are liable to occur.

[0083]

As described above, as compared with conventional toners obtained by the simultaneous mixture of positively electrifiable silica fine particles and negatively electrifiable silica fine particles, the toner of the present invention has a uniform electrification property, and has excellent effects such that a uniform electrification property and excellent flowability are stably maintained for a long period of time by restraining the liberation of negatively electrifiable and/or positively electrifiable silica fine particles.

[0084]

The toner of the invention can be used in any type of image-forming apparatus, e.g., image-forming apparatus using one-component series toners, or image-forming apparatus using two-component series toners, may be used. Image-forming apparatus of a contact development system or image-forming apparatus of a non-contact development system may also be used. Image-forming apparatus of a contact

development system using one-component series toners capable of using the toner of the invention are described in detail, e.g., in patent literature 13. The image-forming apparatus of the present invention is equipped with at least a latent image carrier on which an electrostatic latent image is formed represented by a photosensitive material; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier represented by a developing roller; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier. The toner of the present invention is held in a toner holder, carried from the toner holder to the developing roller (the toner carrier) and supplied to the photosensitive material (the latent image carrier) via the developing roller (the toner carrier), transferred, thereby an image is formed. The toner regulating member adjusts the amount of the toner so that an excess amount of the toner is not supplied to the photosensitive material (the latent image carrier) from the developing roller (the toner carrier).

[0085]

[Example]

The present invention is illustrated with reference

to examples below.

[0086]

(Preparation of toner mother particles)

One hundred (100) mass parts of a styrene-acrylic-based binding resin, 3.5 mass parts of a red pigment (C.I. 12055), and 1.0 mass part of chromium salicylate complex were put into Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED), and homogeneously blended. The mixture was melt-kneaded with a two-shaft kneading extruder PCM-30 (manufactured by IKEGAI KASEI CO., LTD), and after cooling, pulverized by jet air with a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION). The pulverized product was classified with a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), to thereby prepare toner mother particles having a volume average particle size of 8.5 μm.

[0087]

(External additives)

The external additives externally added to toner mother particles in Examples are shown in Table 1 below.

[0088]

Table 1

	External Additive	Trade Name		Average Particle Size	Manufacturer
a1	Negatively electrifiable silica	Negatively electrifiable hydrophobic silica	RX200	15 nm	Nippon Aerosil Co., Ltd.
a2	Negatively electrifiable silica	Negatively electrifiable hydrophobic silica	RX50	40 nm	Nippon Aerosil Co., Ltd.
b	Positively electrifiable silica	Positively electrifiable hydrophobic silica	NA50H	30 nm	Nippon Aerosil Co., Ltd.

[0089]

(External addition process)

In the examples of the present invention, external addition process in each process was performed by adding prescribed amounts of external additives to 100 mass parts of toner mother particles, and stirring the constituents by using a Henschel Mixer FM20B (a product of MITSUI MINING COMPANY, LIMITED) for 3 minutes with Z0S0 type stirring blades at 2,000 rpm. For instance, in process (1), negatively electrifiable silica fine particles were added to toner mother particles and subjected to stirring process with a Henschel Mixer FM20B on the same condition as above, in the next place positively electrifiable silica fine particles in a prescribed amount to 100 mass parts of the toner mother particles were added to the toner mother particles obtained in process (1) to which negatively electrifiable silica fine particles were externally added, and subjected to stirring process with a Henschel Mixer FM20B on the same condition as above.

[0090]

(EXAMPLE 1: Preparation of toner A)

Toner A was prepared by the external addition process of adding 1 mass part of RX200 to 100 mass parts of the above-obtained toner mother particles (process (1)), and by the external addition process of adding 0.5 mass

parts of NA50H to the product obtained in process (1) (process (2)). The process is described in Table 2 below.

[0091]

(EXAMPLE 2: Preparation of toner B)

Toner B was prepared by the same external addition process as in Example 1, except for adding 0.5 mass parts of RX200 (small particle size silica) to 100 mass parts of the toner mother particles and 0.5 mass parts of RX50 (large particle size silica) at the same time in place of adding 1 mass part of RX200. The process is described in Table 2 below.

[0092]

(COMPARATIVE EXAMPLE 1: Preparation of toner C)

Toner C of Comparative Example 1 was prepared by the same external addition process as in Example 1, except for adding 1.0 mass part of RX200 and 0.5 mass parts of NA50H to 100 mass parts of the toner mother particles. The process is described in Table 2 below.

[0093]

(COMPARATIVE EXAMPLE 2: Preparation of toner D)

Toner D of Comparative Example 2 was prepared by the same external addition process as in Example 1, except for replacing process (1) and process (2) in Example 1, i.e., adding RX200 after NA50H. The process is described in Table 2 below.

[0094]

Table 2

	External Additives			Order of External Addition		
	a1	a2	b	First Stage	Second Stage	
Example 1	1.0	-	0.5	a1	b	Toner A
Example 2	0.5	0.5	0.5	a1+a2	b	Toner B
Comparative Example 1	1.0	-	0.5	a1+b	-	Toner C
Comparative Example 2	1.0	-	0.5	b	a1	Toner D

The numeral in the column of External Additives shows the addition amount (mass parts) to 100 mass parts of toner mother particles.

[0095]

(Evaluation of toners A to D)

The toners A to D respectively obtained by the above methods (Table 2) were evaluated. Items and methods of evaluations are as follows.

[0096]

1. Liberation rate of external additives (silica fine particles, titanium oxide fine particles):

The liberation rate of external additives (silica fine particles and titanium oxide fine particles) was measured with PT1000 Particle Analyzer (a product of Yokogawa Electric Corporation). The details of measuring method of the liberation rate of external additives are disclosed in patent literature 7 (JP-A-2002-202622).

Describing the principle in brief, liberation rate is obtained by introducing toner particles into plasma, exciting the toner particle to emit light, and measuring the intensity and time of the emission. For example, toner particles to which external additive SiO_2 has been added are introduced into plasma, and the emission intensity of SiO_2 in the toner particles is measured. Assuming that the toner particle to which SiO_2 has been externally added is a spherical particle, the particle size of the spherical particle (equivalent particle size) is obtained from the emission intensity. Similarly to the case of the toner particle, the equivalent particle size of the liberated SiO_2 can be obtained from the emission intensity. However, since the emission intensity of the liberated SiO_2 is small, the equivalent particle size is small. Accordingly, the liberated external additive can be distinguished from the toner particles by comparing equivalent particle sizes. Therefore, the liberation rate of SiO_2 can be obtained according to the following equation (X), by obtaining all the detected number of external additive SiO_2, and taking the number of individuals having smaller equivalent particle size as the number of particles of the liberated external additive.

[0097]

[mathematical formula 1]

$$\text{Liberation rate} = (\text{detected number of liberated external additive/all detected number of external additive}) \times 100\ (\%) \qquad (X)$$

[0098]

Whether SiO_2 is adhered to a toner particle or liberated is distinguished by making use of the fact that SiO_2 adhered to a toner particle emits light synchronously with the toner particle, but SiO_2 which is not adhered to a toner particle does not radiate synchronously with the toner particle and the time of emission deviates from that of the toner particle (asynchronously). On the basis of the measured value, the liberation rate can be obtained by the following equation (Y).

[0099]

[mathematical formula 2]

$$\text{Liberation rate} = (\text{asynchronous count of external additive/asynchronous count + synchronous count of external additive}) \times 100\ (\%) \qquad (Y)$$

[0100]

A method represented by equation (Y) was adopted in the present invention. The volume average particle size of toner mother particles can also be obtained, e.g., by making a colorant contained in the toner mother particles emit light in plasma, and obtaining the equivalent particle size.

[0101]

2. Electrification characteristics of toner

Electrification characteristics of a toner were judged synthetically by the uniformity of electrification and the rate of occurring of positively electrified toner.

[0102]

(Uniformity of electrification)

The quantity of electrification of a toner is measured as follows with E-SPART Analyzer (manufactured by HOSOKAWA MICRON CORPORATION). Each of the toners prepared in Examples and Comparative Examples and carrier (KBN100 ferrite carrier manufactured by Hitachi Metals, Ltd.) were mixed and stirred, to thereby electrify the toner. Nitrogen gas was then blown to the mixture of the toner and the carrier to separate the toner and the carrier. In the next place, the quantity of electrification of every toner (Q/m) was measured, and the distribution of the quantities of electrification of the toners was obtained, and thereby numbers of the negatively electrified toner and the positively electrified toner.

[0103]

The uniformity of electrification is judged as follows. In number distribution of the quantity of electrification of every one toner (Q/m), the difference between the quantity of electrification of the maximum

frequency (Q_1/m_1) and the value obtained by dividing the total quantity of electrification of the measured toners by the measured count (the number) (Q_2/m_2), i.e., the smaller the absolute value of (Q_1/m_1) - (Q_2/m_2), the sharper is the distribution of the quantity of electrification (uniform), and the greater the absolute value of (Q_1/m_1) - (Q_2/m_2), the broader is the distribution of the quantity of electrification (nonuniform).

[0104]

(Occurring rate of positively electrified toner particles (occurring rate of positive toner (%)))

The number of positively electrified toner particles (%) to the total number of toners measured (measurement count) was obtained as the occurring rate of positive toner (%). The occurring rate of positively electrified toner particles is preferably the smaller, considering the uniformity of electrification of the toner.

[0105]

Judging the uniformity of electrification and the rate of occurring of positively electrified toner synthetically, the smaller the absolute value of (Q_1/m_1) - (Q_2/m_2), and the smaller the occurring rate of positively electrified toner particles (occurring rate of positive toner (%)), the better is the electrification characteristics of the toner.

[0106]

The results of the above evaluations are shown in Table 3 below. "Liberation Rate of Si in First Stage (%)" in Table 3 is the liberation rate of the external additives obtained by taking out a sample after the process in the first stage in Table 2, and "Liberation Rate of Si in Second Stage (%)" is the liberation rate of the external additives obtained by taking out a sample after the process in the second stage in Table 2. "Liberation Rate of Si in Second Stage (%)" is the liberation rate of the external additives of the toner as a whole. That is, "Liberation Rate of Si in Second Stage (%)" is the liberation rate of the total of the negatively electrifiable silica fine particles and the positively electrifiable silica fine particles (hereinafter referred to as the total liberation rate of positive/negative silica fine particles) liberated in the toner. Accordingly, the liberation rate of the positively electrifiable silica fine particles is presumed by subtracting the liberation rate of Si of the sample processed in process (1) from the total liberation rate of Si of positive/negative silica fine particles.

[0107]

Table 3

		Liberation Rate of Si in First Stage	Liberation Rate of Si in Second Stage	a	b	c	Occurring Rate of Toner (%)
				Q_1/m_1 (μC/g)	Q_2/m_2 (μC/g)	a-b (μC/g)	
Example	Toner A	0.24	0.50	-13.56	-15.38	1.82	1.5
Example	Toner B	0.29	0.55	-12.44	-15.11	2.67	2.1
Comparative Example	Toner C	0.82	-	-12.66	-18.32	5.66	6.2
Comparative Example	Toner D	0.31	0.93	-18.99	-26.52	7.53	7.1

[0108]

As is apparent from the results in Table 3, the liberation rate of Si in the second stage, i.e., the total liberation rate of positive/negative silica fine particles, of toner A (Example 1) and toner B (Example 2) obtained by the external addition of negatively electrifiable silica fine particles and positively electrifiable silica fine particles in this order was from 0.50 to 0.55%. On the other hand, the total liberation rate of positive/negative silica fine particles of toner C (Comparative Example 1) obtained by the external addition of negatively electrifiable silica fine particles and the positively electrifiable silica fine particles at the same time was 0.82%, and the total liberation rate of positive/negative silica fine particles of toner D (Comparative Example 2) obtained by the external addition of positively electrifiable silica fine particles and negatively electrifiable silica fine particles in this order was 0.93%. The values in Comparative Examples 1 and 2 are far higher as compared with those in Examples 1 and 2.

[0109]

Since the liberation rates of the positively electrifiable silica fine particles in Examples 1 and 2 are presumed by (the liberation rate of Si in the second stage) - (the liberation rate of Si in the first stage), the

values are both thought to be about 0.26%. Contrary to this, the liberation rate of the positively electrifiable silica fine particles of the toner in Comparative Example 2 is 0.31%, and the liberation rate of the negatively electrifiable silica fine particles is presumed to be: 0.93 - 0.31 = 0.62(%). The liberation rate of the negatively electrifiable silica fine particles of the present invention is thus extremely low. This shows that negatively electrifiable silica strongly adheres to toner mother particles, in the relationship of the work function, by performing external addition process of negatively electrifiable silica fine particles in the first stage.

[0110]

Further, to examine the third value c (a-b) in Table 3, the values c of the toners in Examples 1 and 2 are far smaller as compared with the values in Comparative Examples 1 and 2, which shows that the toners in the present invention are excellent in the uniformity of the quantity of electrification. It is also seen that the occurring rates of positive toner in the toners in Examples 1 and 2 are also far smaller than the occurring rates of positive toner in the toners in Comparative Examples 1 and 2.

[0111]

From these results, the present invention has been improved to be capable of providing toners which are excel-

lent in the uniformity of electrification, small in the occurring rate of positive toner and in a preferred range, so that excellent in electrification characteristics, and excellent in flowability.

[0112]

(EXAMPLE 3: Preparation of toner E)

External addition process was performed by adding 2.0 mass part of RX200 to 100 mass parts of the toner mother particles obtained above (process (1)). Toner E was prepared by the external addition process of adding 0.1 mass part of NA50H to the external addition processed-product obtained in process (1) (process (2)). The liberation rate of Si, the quantity of electrification, and the occurring rate of the positively electrified toner particles (occurring rate of positive toner (%)) of the obtained toner E were evaluated in the same manner as in Example 5. The process is described in Table 4 below.

[0113]

(EXAMPLE 4: Preparation of toner F)

Toner F was prepared in the same process as in Example 1, except for adding 1.0 mass part of RX200 and 1.0 mass part of NA50H to 100 mass parts of the toner mother particles, and toner F was evaluated in the same manner as in Example 6. The results are shown in Table 4 below.

[0114]

(EXAMPLE 5: Preparation of toner G)

Toner G was prepared in the same process as in Example 1, except for adding 4.0 mass parts of RX200 and 0.1 mass part of NA50H to 100 mass parts of the toner mother particles, and toner G was evaluated in the same manner as in Example 6. The results are shown in Table 4 below.

[0115]

(EXAMPLE 6: Preparation of toner H)

Toner H was prepared in the same process as in Example 1, except for adding 0.5 mass parts of RX200 and 1.0 mass part of NA50H to 100 mass parts of the toner mother particles, and toner H was evaluated in the same manner as in Example 6. The results are shown in Table 4 below.

[0116]

Table 4

		External Additives		Liberation Rate of Si after Process (1)	Liberation Rate of Si after Process (2)	a	b	c	Occurring Rate of Toner
		Process (1)	Process (2)			Q_1/m_1 (μC/g)	Q_2/m_2 (μC/g)	a-b (μC/g)	
Example 3	Toner E	2.0	0.1	0.44	0.44	-15.21	-17.33	2.12	2.2
Example 4	Toner F	1.0	1.0	0.29	0.55	-13.36	-16.38	3.02	2.6
Example 5	Toner G	4.0	0.1	0.66	0.74	-17.65	-23.10	5.35	1.8
Example 6	Toner H	0.5	1.0	0.24	0.76	-13.11	-14.98	1.87	5.9

The numeral in the column of External Additives shows the addition amount (mass parts) to 100 mass parts of toner mother particles.

[0117]

In Examples 3 to 6, examination was performed by changing the proportion of addition amounts of negatively electrifiable silica fine particles and positively electrifiable silica fine particles. In Examples 3 and 4, the ratios of the amount of negatively electrifiable silica fine particles/the amount of positively electrifiable silica fine particles are respectively set at 20/1 and 1/1 so as to come to the range of 1/1 to 30/1. In Example 5, the ratio is 40/1, and in Example 6 the ratio is 1/2.

[0118]

From the results in Table 4, the Si liberation rate after process (2) is small, the uniformity of electrification is excellent, and the occurring rate of positively electrified toner particles is in a preferred range when the ratio of the amount of negatively electrifiable silica fine particles/the amount of positively electrifiable silica fine particles is in the range of 1/1 to 30/1 as in the toners in Examples 3 and 4 (toner E and Toner F). Since toner G in Example 5 was high in this ratio and the absolute amount of the negatively electrifiable toner added was large, the Si liberation rate after process (2) was a little high, and the uniformity of electrification was a little inferior to toner F but there was no problem in using the toner. Since the amount of the

negatively electrifiable silica fine particles in toner H in Example 6 was comparatively small, the Si liberation rate after process (2) of toner H was high, and a little inferior to toner E and toner F in the uniformity of electrification, there was no problem in using the toner.

[0119]

[Effect of the Invention]

The toner obtained by externally adding negatively electrifiable silica fine particles and positively electrifiable silica fine particles in this order to toner mother particles is excellent in the uniformity of electrification, small in the occurring rate of positive toner, so that excellent in electrification characteristics, and excellent in flowability.

[Designation of Document] ABSTRACT

[Abstract]

[Problem] To provide a toner which is low in desorption of silica fine particles, which can maintain the electrification property for a long period of time, shows high flowability.

[Means for Solving the Problem] The toner of the present invention can be obtained by externally adding negatively electrifiable silica fine particles and positively electrifiable silica fine particles in this order to toner mother particles. Preferably, the negatively electrifiable silica fine particles comprise two kinds of negatively electrifiable silica fine particles each having a different average particle size, and the addition ratio of the negatively electrifiable silica fine particles having a large average particle size to the negatively electrifiable silica fine particles having a small average particle size is 1/3 to 3/1 in a mass ratio, and the blending ratio of the negatively electrifiable silica fine particles to the positively electrifiable silica fine particles is from 1/1 to 30/1 in a mass ratio. A toner further excellent in electrification characteristics, and excellent in flowability can be provided by externally adding negatively electrifiable silica fine particles and positively

electrifiable silica fine particles to toner mother particles in this proportion.

[Representative Drawing] none